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The Crystal Structure of Dihydroxyfumaric Acid Dihydrate

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Dihydroxyfumaric acid dihydrate $C_4H_4O_6.2H_2O$ is monoclinic, $a=6{\cdot}40$, $b=13{\cdot}03$, $c=5{\cdot}34$ Å; $\beta=126{\cdot}5°$. Space group $P2_1/c$, two centrosymmetric molecules in the unit cell. The atomic positions were determined by the [100], [010], [001] projections and by least-squares refinement of X-ray diffraction data. In the crystal structure the dihydroxyfumaric acid molecules are arranged in sheets, alternate sheets being separated by 1·60 Å. The binding of the sheets of molecules in alternate layers is provided *via* the water molecules which are linked through oxygen atoms of the COOH groups (O–H···O) by hydrogen bonds of 2·56 and 2·85 Å. The molecule is nearly planar with generally accepted bond lengths and angles.

Dihydroxyfumaric acid $C_4H_4O_6.2H_2O$ has of late assumed importance in biochemistry and has variously been described in the past as having either the *cis* or the *trans* configuration. Chemical evidence for or against these alternative configurations has been presented by Hartree (1953). In a previous communication the senior author (Gupta, 1953) was able to show conclusively from X-ray diffraction data that the molecule in the crystalline state must have the *trans* configuration since it crystallized in the monoclinic system, class $2/m$, space group $P2_1/c$ with two molecules in the unit cell of dimensions,

$$a=6{\cdot}40\pm0{\cdot}02,\ b=13{\cdot}03\pm0{\cdot}03,\ c=5{\cdot}34\pm0{\cdot}01\ \text{Å};\quad \beta=126{\cdot}5\pm0{\cdot}1°.$$

The observed density is 1·715 g.cm^{-3}, calculated 1·708 g.cm^{-3}. The systematic absences of the X-ray reflexions are: $h0l$ absent when l is odd and $0k0$ absent when k is odd, so that the space group is determined uniquely as $P2_1/c$. Details of crystal morphology and pseudo-orthorhombic symmetry displayed by the crystal are given by Gupta (1953).

In a preliminary note Gupta (1955) gave the results of a Fourier analysis of the $0kl$ data from the dihydroxyfumaric acid dihydrate crystal. The structure determination, however, remained incomplete for more than nine years. The present paper, therefore, describes the results of fresh investigation by the authors using new experimental data.

Table 1. *Final atomic coordinates and standard deviations*

	x/a	$\sigma(x)$ (Å)	y/b	$\sigma(y)$ (Å)	z/c	$\sigma(z)$ (Å)
C(1)	0·0880	0·014	0·0112	0·013	0·1516	0·011
C(2)	0·2162	0·013	−0·0696	0·012	0·3970	0·012
O(1)	0·3426	0·010	−0·0354	0·009	0·6748	0·010
O(2)	0·1980	0·010	−0·1603	0·008	0·3182	0·008
O(3)	0·1147	0·009	0·1097	0·008	0·2689	0·008
$O_4(H_2O)$	0·4296	0·009	0·1777	0·009	0·9164	0·008

Experimental

Crystals of dihydroxyfumaric acid dihydrate were grown from a solution of glass-distilled water and dry acetone which was left overnight in a refrigerator. They appeared as thin diamond-shaped colourless plates with (010) as the platy face. Reflexions $0kl$, $hk0$ and $h0l$ were collected by normal beam Weissenberg photography using multiple-film technique and Cu unfiltered radiation. To obtain a range of intensity for each reflexion, exposures were given for different lengths of time. Reflexions were observed to a sin θ limit of 0·973. Small crystals were used and absorption errors are negligible (linear absorption coefficient for Cu $K\alpha$ radiation 17·6 cm^{-1}). The intensities of the spots were estimated visually using an intensity scale with graded series of crystal reflected spots.

Determination and refinement of the structure

Since there are only centrosymmetric molecules in the space group $P2_1/c$, the asymmetric unit for the purpose of crystal structure determination may be taken as $C_2H_2O_3.H_2O$. The structure will be determined by thirty parameters but if one excludes the hydrogen atoms the number of unknown parameters becomes eighteen only. The structure was solved by a study of the Patterson maps for the three projections including modified sharpened Patterson syntheses using functions similar to those of Carpenter & Donohue (1950). Trial-and-error methods were used in the last resort to fix the orientation of the molecule which confirmed that the structure postulated earlier by Gupta (1955) was correct in gross features but major shifts in some atomic positions were indicated. The process of reiterative refinement by normal Fourier technique was employed after this stage. The final electron-density maps with projection down the [100], [001] and [010] axes are shown in Figs. 1, 2 and 3 respectively. The resolution for the [100] and [001] projection is very good with all the atoms well resolved or nearly so.

The structure was then refined by a diagonal least-squares procedure but using only an isotropic temperature factor of $B=2·1$ Å^2 for the $0kl$, $B=2·5$ Å^2 for the $hk0$ and $B=2·1$ Å^2 for the $h0l$ reflexions.

The final values of the reliability index, R, for the $0kl$, $hk0$ and $h0l$ reflexions are 11·6%, 14·0% and 13·5% respectively. In calculating these values of R, only isotropic temperature factors as given above and atomic scattering factors for carbon and oxygen taken from *International Tables for Crystallography* Vol. III were used. Unobserved reflexions were given the value of half minimum observed structure amplitude (Wilson, 1949). In the $hk0$ structure amplitudes, reflexions 200 and 310 have been excluded and in the $h0l$ structure amplitudes reflexion 200 has been excluded as they probably suffer from extinction. If the unobserved reflexions are taken to be zero, the R values become, $R(0kl)=12·4\%$, $R(hk0)=14·8\%$ and $R(h0l)=13·8\%$.

The final coordinates of the atoms together with their standard deviations $\sigma(x), \sigma(y), \sigma(z)$ are listed in Table 1. Standard deviations of the coordinates have been cal-

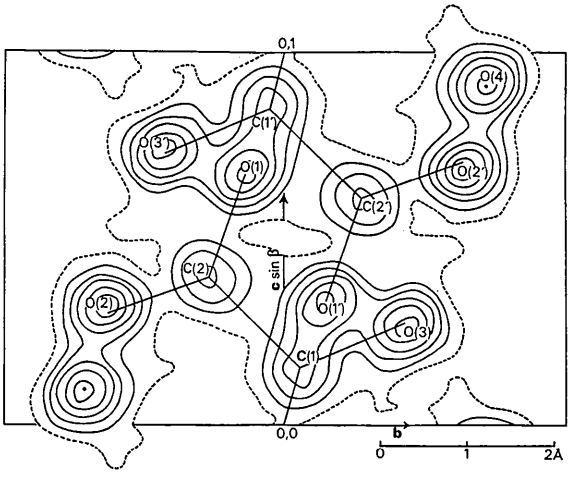

Fig. 1. Electron density projection along [100].

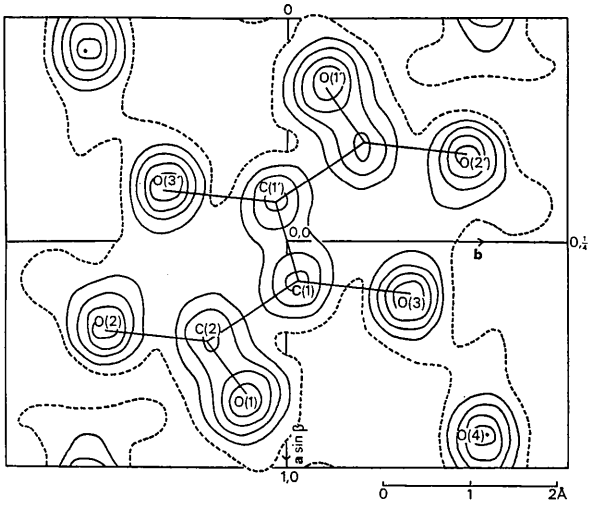

Fig. 2. Electron density projection along [001].

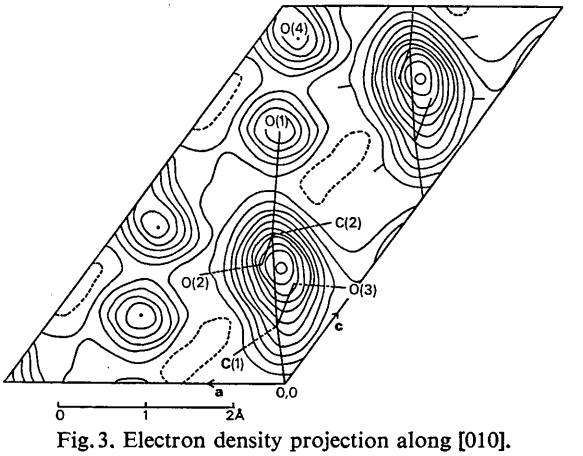

Fig. 3. Electron density projection along [010].

culated from the formula given in equation (1) of Ibers & Cromer (1958), using unit weights. The symbols refer to the atoms shown in Fig. 1.

The bond lengths and angles are shown in Table 2 together with the standard deviations calculated with the formula given by Ahmed & Cruickshank (1953). There is also an additional uncertainty of about 0·3% in the absolute values of the bond lengths owing to experimental error in measuring the unit-cell constants, but this will not affect their relative values.

Table 2. *Bond lengths and angles, and standard deviations*

Bond lengths		Standard deviations
C(1)–C(1′)	1·34 Å	0·045 Å
C(1)–C(2)	1·49	0·016
C(1)–O(3)	1·39	0·015
C(2)–O(1)	1·28	0·013
C(2)–O(2)	1·24	0·014

Table 2 (*cont.*)

Bond angles		Standard deviations
C(1′)–C(1)–C(2)	122° 19′	55′
C(2)–C(1)–O(3)	113 37	44
O(3)–C(1)–C(1′)	122 13	53
C(1)–C(2)–O(1)	114 20	50
O(1)–C(2)–O(2)	126 39	50
O(2)–C(2)–C(1)	110 02	51

The standard deviation in electron density of (ϱ) calculated with the use of expressions given by Cruickshank (1949) is given in Table 3.

Table 3. *Standard deviations in electron density*

Projection	$\sigma(\varrho)$
(0*kl*)	0·309 e.Å^{-2}
(*hk*0)	0·341
(*h*0*l*)	0·469

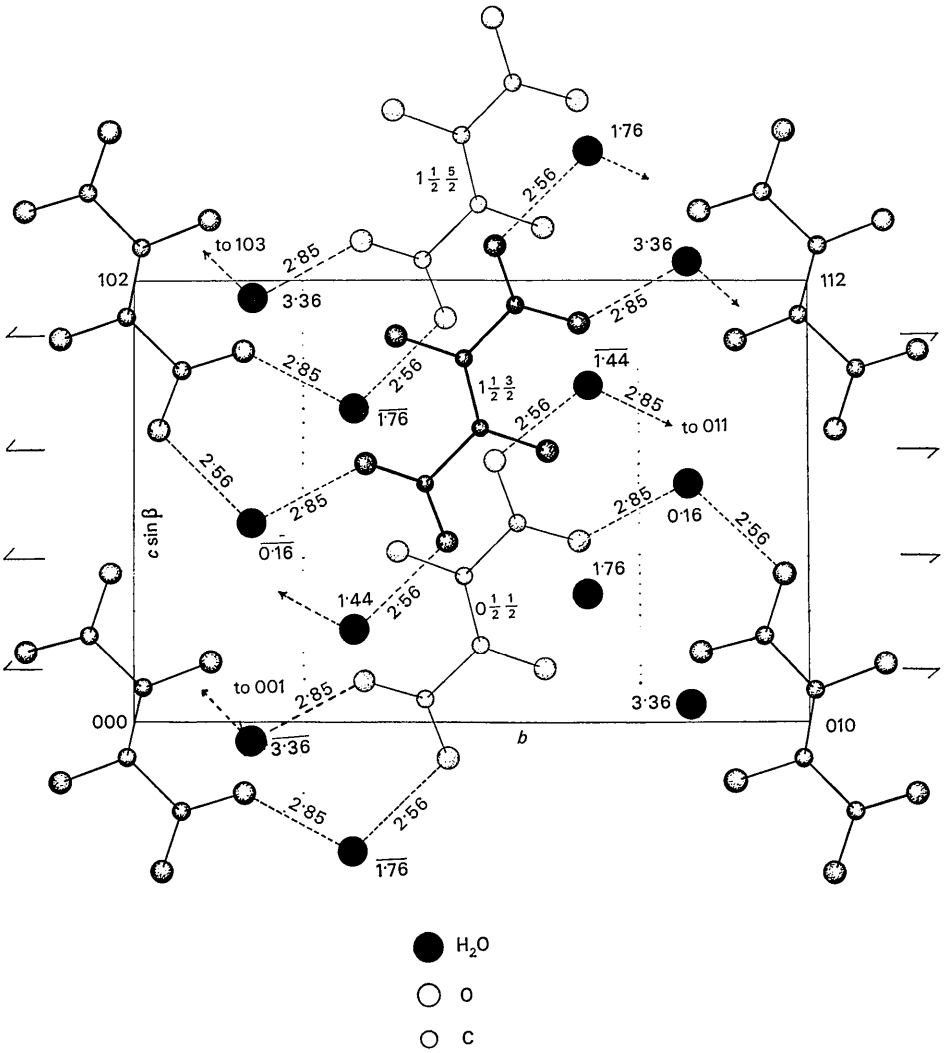

Fig. 4. Crystal structure looking down the [100] axis. The molecules in different sheets are shaded to show their relative sequence, the topmost being with the heaviest shading. The heights of water molecules in Å from the plane of projection are shown.

The bond lengths and angles are normal and agree well with generally accepted values, and are also similar to those found in other dicarboxylic acids. The carbon–hydroxyl bond is also normal. The peak heights, ϱ_m, of the atoms in the [100] and [001] projections using a Gaussian function over nine points mesh and method of least squares are given in Table 4.

Table 4. *Electron density peak heights*

	[100] projection	[001] projection
C(1)	9·49 e.Å^{-2}	8·72 e.Å^{-2}
C(2)	8·78	8·59
O(1)	13·21	12·23
O(2)	13·52	10·44
O(3)	13·55	12·06
O(4)	13·04	11·20

Planarity of the molecule

The equation to the best plane passing through all the ten atoms in the molecule was determined by the method of least squares and was found to be

$$x'+0{\cdot}10410y'-0{\cdot}01302z'=0\,.$$

The coordinates x', y', z' are referred to orthogonal axes and are related to the crystallographic axes in the following way:

$$x'=x+z\cos\beta,\ y'=y,\ z'=z\sin\beta\,.$$

The deviations δ of the atoms from the best plane along with the standard deviation $\sigma(\delta)$ of the deviation δ are given in Table 5.

Table 5. *Deviation, δ, of atoms from best plane, and standard deviation of δ*

	δ	$\sigma(\delta)$
C(1)	0·087 Å	0·0151 Å
C(2)	0·006	0·0149
O(1)	−0·036	0·0114
O(2)	0·021	0·0109
O(3)	0·014	0·0105

The deviations of atoms C(1) and O(1) from the molecular plane are significant. The distances from the oxygen atom O(1) of the molecule at (0,0,0) to the atoms C(1′) and O(3′) of the molecule at (0,0,1) are 3·40 and 3·26 Å respectively. This probably indicates

Table 6. *Orientation of the molecule with respect to the crystallographic axes*

Molecular axis	Angle with the *a* axis	Angle with the *b* axis	Angle with the *c* axis	Direction cosines *l*	*m*	*n*
L	83°4′	77°27′	14°21′	0·1205	0·2173	0·9688
M	83 58	166 43	78 9	0·1040	—0·9733	0·2053
N	6	84 4	90 44	0·9945	0·1035	−0·0129

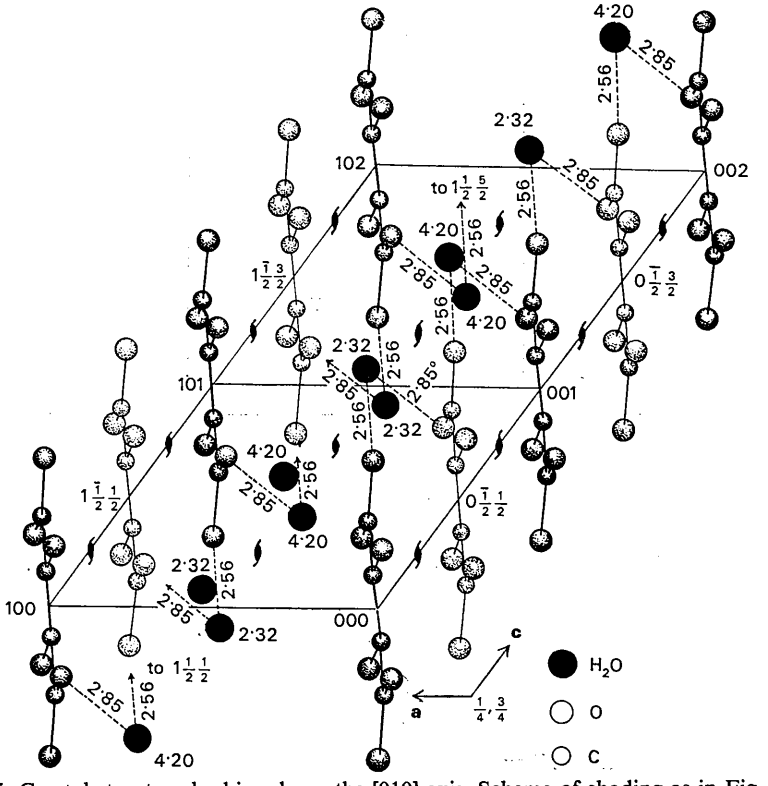

Fig. 5. Crystal structure looking down the [010] axis. Scheme of shading as in Fig. 4.

that the oxygen atom O(1) is attracted by the atoms C(1′) and O(3′) and may explain the lack of planarity due to intermolecular attraction.

The orientation of the molecule with respect to the crystallographic axes is given in Table 6, where the L, M, N axes are defined as follows. The L axis is the axis passing through the central C=C bond, the M axis is perpendicular to the L axis and in the plane of the molecule, assumed planar, and the N axis is perpendicular to both the L- and the M-axis of the molecule.

Description of the structure

Figs. 4 and 5 show the crystal structure as seen along the [100] and [010] axes respectively. In the crystal, dihydroxyfumaric acid molecules are arranged in extensive chains parallel to the [102] direction. The extensive chains are themselves in turn arranged in sheets, approximately normal to the a axis, alternate layers having a separation of 1·60 Å ($\simeq a/4$). The sheets of molecules are stacked parallel to each other but having a relative displacement of $(\mathbf{b}+\mathbf{c})/2$ between any two adjacent layers. The nearest distance of approach between two neighbouring molecules in the same chain is through an oxygen–oxygen contact of 2·94 Å. The water molecules play a dominant role in binding the sheets of dihydroxyfumaric acid molecules. The water molecules are so arranged that they are sandwiched in between the layers of the dihydroxyfumaric acid molecules cross-linking on either side of it, two sheets of molecules forming adjacent layers. This cross-linking is through short hydrogen bonds of 2·56 and 2·85 Å, the linkage being *via* the water molecules of the type O(1)–H_2O and H_2O–O(2) where O(1) and O(2) are oxygen atoms belonging to the COOH groups of two *different* dihydroxyfumaric acid molecules in *adjacent* layers. In effect, the two oxygen atoms in each carboxyl groups of the same molecule are linked *via* two different water molecules to the oxygen atoms of the COOH groups of the molecules either in the layer above or in the layer below. The water molecules themselves may be supposed to be located at the crests of a sine curve oriented to run parallel to the c crystallographic axis somewhat resembling a 'flattened' spiral, making roughly an angle of 54° with the normal to the sheets of the molecules in the crystal. Apart from the distances of 2·56 and 2·85 Å between the water molecules and the oxygen atoms of the COOH group there is another distance of 2·97 Å, also between a water molecule and one of the oxygen atoms of the COOH group, as shown in Fig. 6. The nearest distances between the oxygen atoms of the hydroxyl group and water molecules are 2·92 and 3·28 Å. The nearest distance between two water molecules is 3·27 Å. All other distances of contact between two neighbouring molecules in different layers are greater than 3·0 Å.

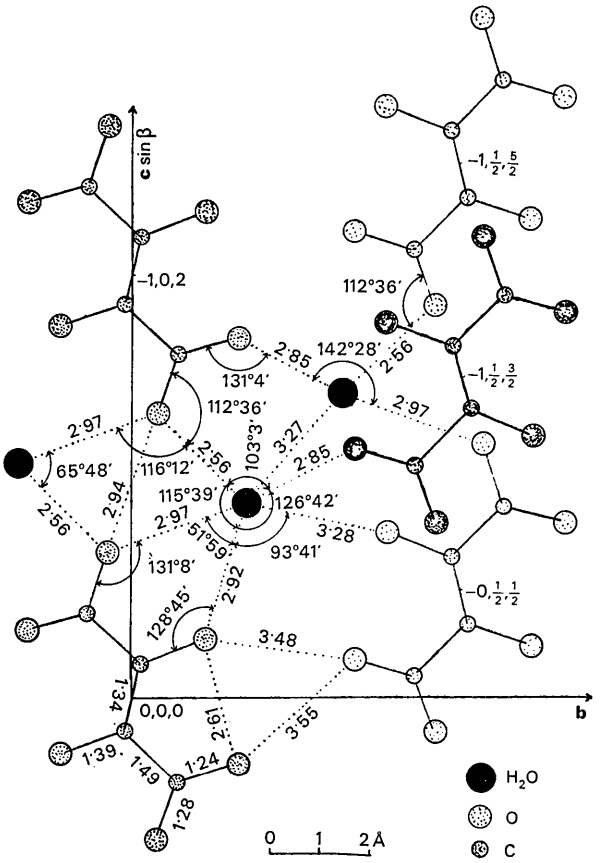

Fig. 6. The scheme of hydrogen bonding with the values of angles and interatomic distances.

The coordination number defined as the number of molecules having one or more contacts with the reference molecule is 12, distances exceeding 3·40 Å having been excluded in fixing the coordination number.

The water molecules make as many as 8 contacts with surrounding oxygen atoms if the 'contact distance' is limited to 3·5 Å or less.

There are four hydrogen atoms per molecule and all of them are utilized for the formation of hydrogen bonds in the crystal structure, as may be seen from Fig. 6. Fig. 7 shows an $(F_o - F_c)$ synthesis for the [100] axis projection in which the contributions of the oxygen and carbon atoms only have been subtracted. There are four well resolved peaks indicated as A, B, C and D. Although the positions of the hydrogen atoms have not been fixed with certainty it seems fairly certain that the probable hydrogen bonds are those which account for the presence of these peaks. The distance 2·56 Å accounts for two hydrogen bonds per molecule. The distance 2·85 Å accounts for another two hydrogen bonds. The distance of 2·61 Å between oxygen atoms O(3) and O(2′) accounts for the remaining two intramolecular hydrogen bonds in the molecule.

The list of observed and calculated structure factors can be obtained from the authors on request.

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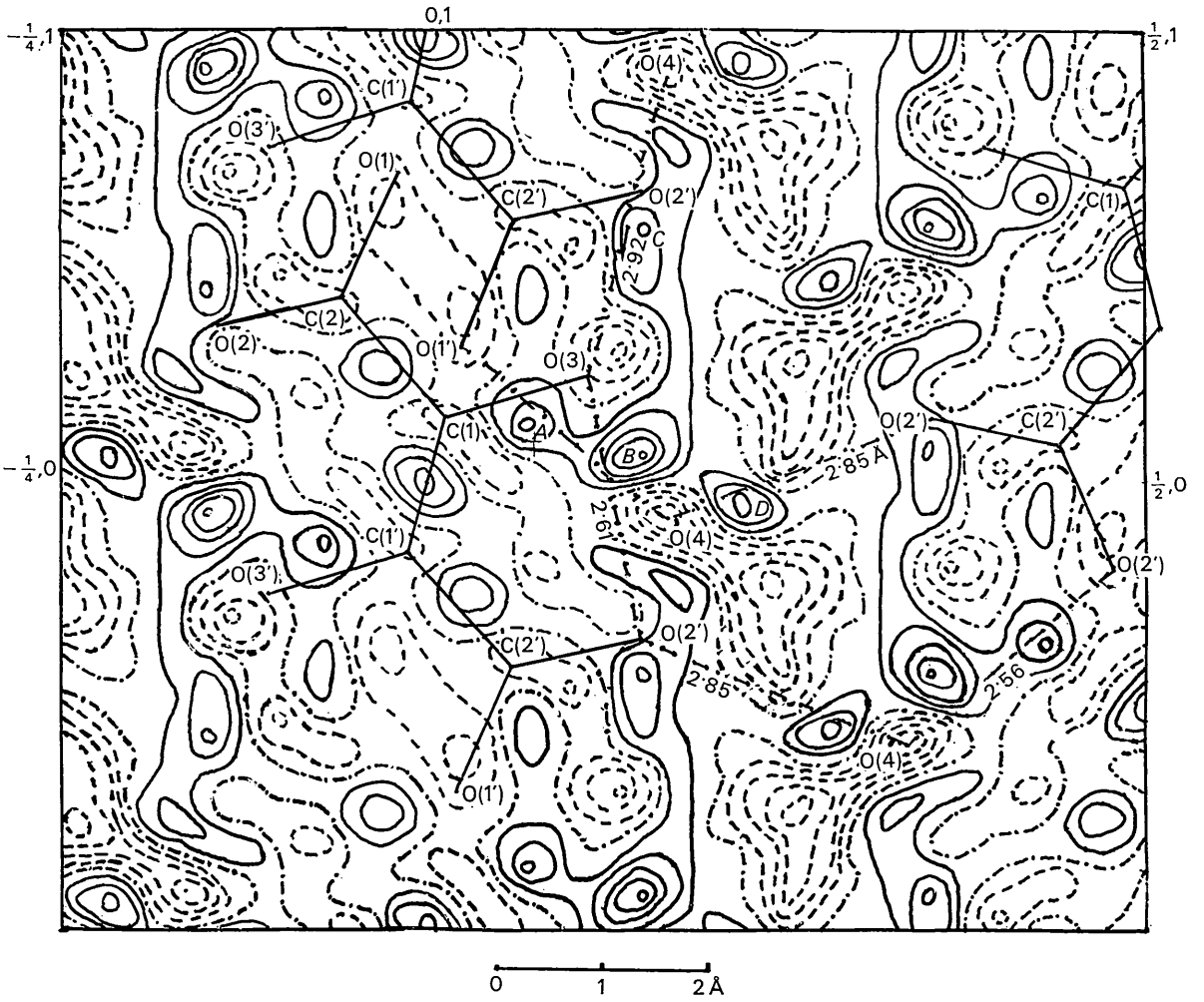

Fig. 7. $(F_o - F_c)$ synthesis for the projection along [100]. Only the contributions of the oxygen and carbon atoms have been subtracted.

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